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**Addendum to the  
Preliminary Draft  
Remedial Investigation Report  
--Dioxin/Furan Analysis of Ash--  
C&D Recycling Site  
Luzerne County, Pennsylvania**

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**AR305540**

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## 1.0 INTRODUCTION

This document serves as an addendum to the Fred C. Hart Associates, Inc. (HART) report entitled *Preliminary Draft Remedial Investigation Report, C&D Recycling Site*, (RI) dated and submitted to the USEPA on January 29, 1990. This report summarizes the collection of ash samples at the C&D Recycling Site (Site), their analysis for the group of organic compounds classified as dioxins and furans, an interpretation of the analytical work and results, and a discussion of the toxicity implications of these compounds at the Site. The need for this addendum was the result of problems associated with the analysis of both sets of ash samples collected in July and November 1989, as described on page 3-5 of the Preliminary Draft RI report.

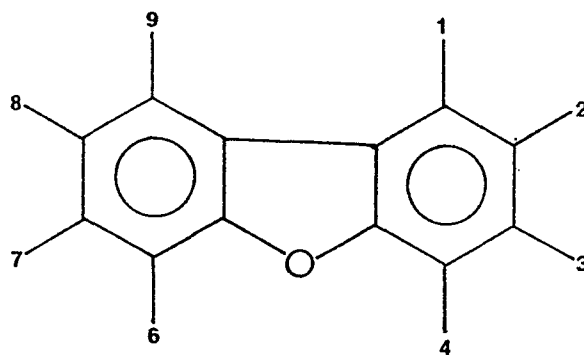
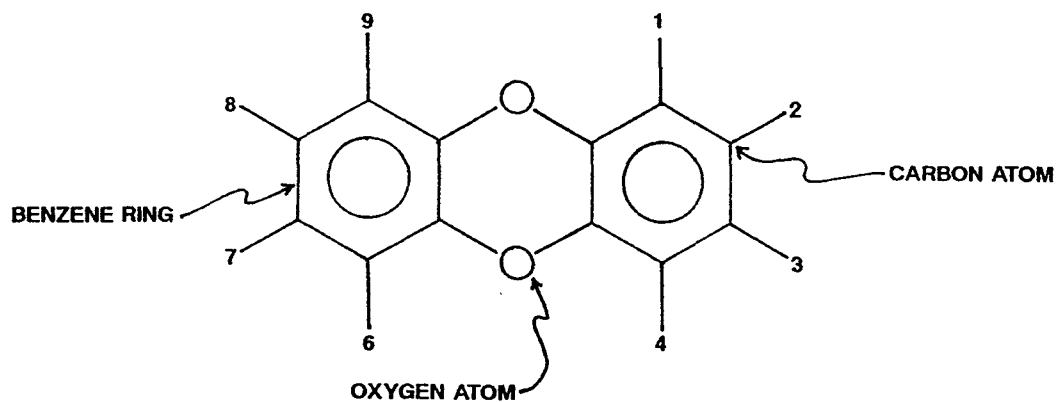
### 1.1 Dioxins and Furans

Dioxin is an abbreviated term for a family of 75 related chemical compounds known as polychlorinated dibenzo-p-dioxins. The dioxin molecule is composed of two benzene rings (six carbon atoms each) linked by two carbon-oxygen-carbon bonds. A schematic representation is shown in Figure 1. This configuration allows for eight sites on the benzene rings, four on each ring, for chlorine substitution and are numbered as shown in Figure 1. For example, the 2378 TCDD isomer (2378 tetrachloro dibenzo-p-dioxin) would have chlorine atoms bonded to the carbon atoms at sites 2, 3, 7, and 8. The remaining four sites (1, 4, 6 & 9) would be occupied by hydrogen atoms. The 75 dioxin compounds are simply variations on the number of chlorine atoms bonded to the two rings and which sites those chlorine atoms are bonded to.

Furan is an abbreviated term for the family of 135 related chemical compounds known as polychlorinated dibenzofurans. As shown in Figure 1, the dibenzofuran molecule is very similar to the dioxin molecule. It is also composed of two benzene rings but unlike dioxin its two benzene rings are linked by one carbon-carbon bond and one carbon-oxygen-carbon bond.

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# DIOXIN



# DIBENZOFURAN

NUMBERS INDICATE BONDING SITES FOR CHLORINE OR HYDROGEN ATOMS

FIGURE 1

CHEMICAL STRUCTURE OF  
DIOXINS AND FURANS

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Dibenzofuran also has eight sites on the benzene rings for chlorine substitution as shown in Figure 1. Because the dibenzofuran molecule is less symmetrical, there are more variations associated with the location of the chlorine atoms and, therefore, can form a greater number of compounds.

Isomers of dioxin and dibenzofuran compounds are those which have the same number of chlorine atoms in their formula. The difference between compounds which are isomers is the location of the chlorine atoms. An example would be tetrachloro dibenzo-p-dioxin which has six isomers. All contain four chlorine atoms but in various positions on the benzene rings: 1, 2, 3, 4; 1, 2, 3, 7; 1, 2, 3, 9; 1, 2, 8, 9; 1, 3, 6, 8; and 2, 3, 7, 8. While all dioxin and dibenzofuran compounds have similar characteristics, the reported toxicity of any particular compound varies widely depending both on the number of chlorine atoms and their relative positions on the benzene rings. Toxicity is also dependent upon whether there are two carbon-oxygen-carbon bonds (dioxin) or just one such bond (dibenzofuran).

## 1.2 Source of Dioxins and Furans

Dioxins and furans are present in very minute quantities throughout the environment. Neither of these compound groups are produced intentionally since they serve no useful purpose. The two main sources of these compounds are byproducts created in the manufacture of other chemical compounds such as pentachlorophenol, PCBs, and certain pesticides, and in the incomplete combustion of material containing chlorine atoms and organic compounds. The latter source includes forest fires and wood stoves, municipal incinerators and motor vehicles. The number and type of the many dioxin and furan compounds produced varies depending on the source. For example, the temperature of the burn and the composition of the material burned are only two of the many factors that affect which dioxin and furan compounds are produced. AR305545

### 1.3 Persistence

Some dioxins and furans are very resistant to breakdown by chemical and biological means. As a result, these compounds can remain in the environment for years. However, most of these compounds can be broken down by sunlight. At the Site, the potential presence of dioxins and furans is due to the furnaces and open burning associated with former activities. Hence, the potential fate of these compounds was into the air with the stack emissions and smoke from burning and in the ash residue. It is most probable that the maximum concentrations of these compounds is contained in the ash residue while the levels in the soils are likely to be very low due to dispersion, dilution, and breakdown by exposure to sunlight.

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## 2.0 SAMPLE COLLECTION

Samples of ash were collected on two separate occasions for dioxin/furan analysis from two ash piles at the Site. The first pile is located northeast of the main facility building and the second is located south of the old furnace in the central portion of the Site. The locations, sampling dates, and sample identifications are shown in Figure 2.

### 2.1 Sampling Rationale

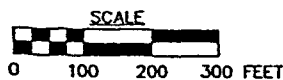
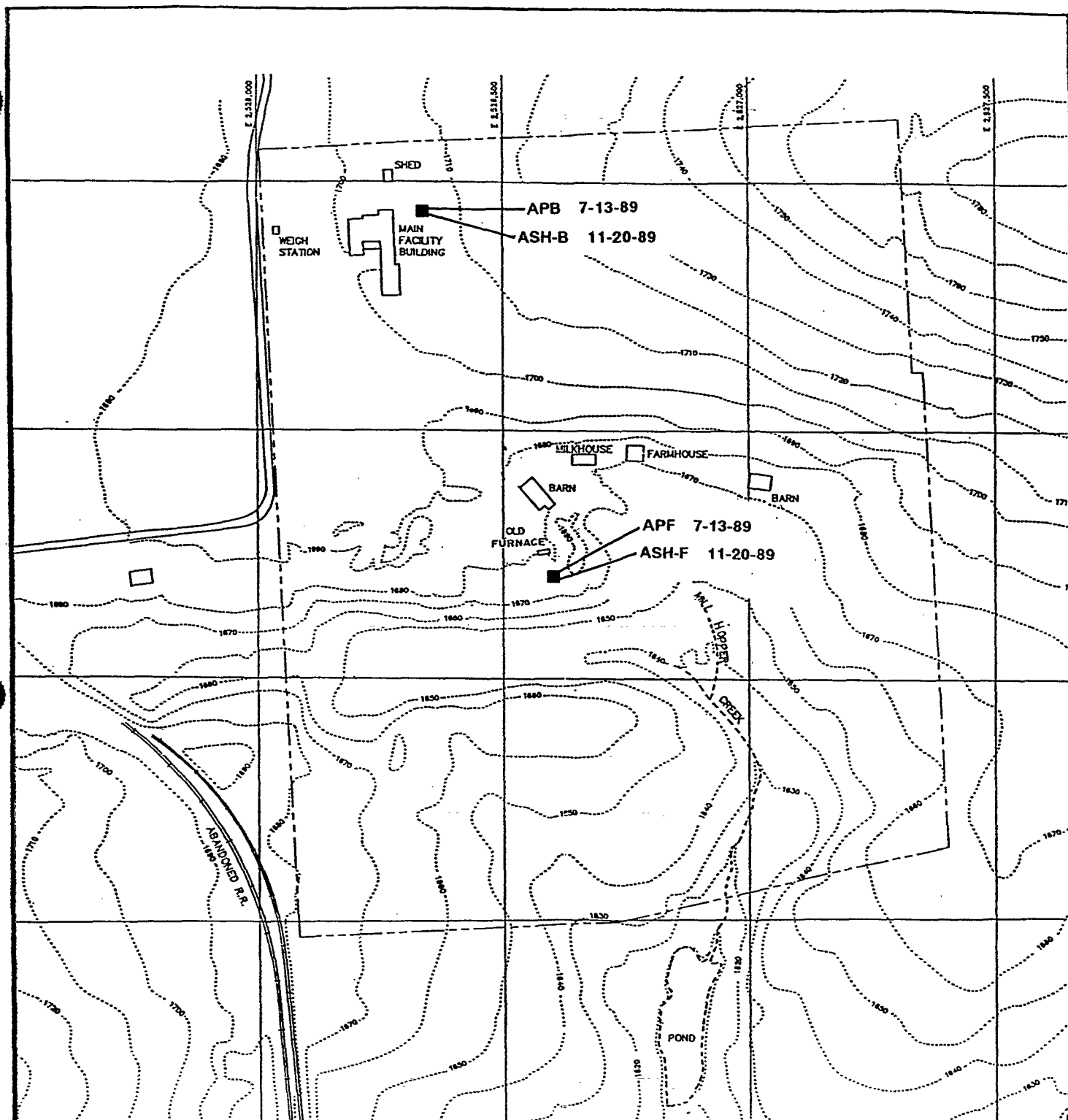
The rationale for targeting the ash for dioxin/furan analysis is that if present at the Site, the highest concentrations of these compounds would most likely be found in the ash residue resulting from the burning process (see Section 1.3 above). By analyzing the ash, the maximum concentration of these compounds at the Site could be determined and a decision could then be made regarding the need for further sampling of other media. Distribution of these compounds to other media, specifically soil, would occur primarily from fallout of stack emissions and suspended ash in surface runoff from the ash piles. However, due to dispersion, dilution, and breakdown via sunlight the concentrations of dioxin and furan compounds in other media is expected to be far below those found in the ash.

### 2.2 July 1989 Sampling

The first ash samples for dioxin/furan analysis were collected on July 13, 1989 from the two piles shown in Figure 2. One grab sample of ash was collected from each pile. All ash piles on the Site have been covered with a one foot layer of soil and several layers of Visqueen (reinforced plastic). These materials were removed and each sample was collected with a clean stainless-steel trowel, mixed in a stainless-steel mixing bowl and then transferred to precleaned laboratory supplied sample containers. The soil and Visqueen covers were then restored over the sampling point. Samples were placed on ice and shipped to CompuChem Laboratories with proper chain of custody documentation.

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ASH  
PILE



KEY  
SAMPLE  
ID

APF

SAMPLING  
DATE

7-13-89

FIGURE 2

ASH SAMPLE LOCATIONS FOR  
DIOXIN/FURAN ANALYSIS

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As described in the above referenced RI report, the laboratory failed to extract and analyze these samples within the time specified in the analytical method. Additionally, only the total concentration for each dioxin and furan isomer group was requested. For these reasons, which will be more fully explained in subsequent sections of this report, a decision was made to resample the two ash piles.

### 2.3 November 1989 Sampling

On November 20, 1989, the same two ash piles were resampled. Both samples were collected in the same manner as described above except that the ash was mixed in place rather than in a mixing bowl. Samples were transported to the same laboratory as described above. In January 1990 the laboratory reported difficulties in the analysis of these samples which prevented inclusion of the results in the Preliminary Draft RI report. A full description of the difficulties encountered during analysis is presented in section 3.2 of this report.

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### 3.0 SUMMARY OF ANALYTICAL WORK

Analytical work for both sets of ash samples was performed by ChemWest Analytical Laboratories, Inc., which is a subsidiary of CompuChem Corporation. All samples were submitted through CompuChem to the ChemWest Laboratory in Sacramento, California under chain-of-custody. Details of the analyses, analytical parameters, difficulties encountered, and QA/QC Summary Sheets will be presented in this section.

#### 3.1 July 1989 Samples

Ash samples collected on July 13, 1989 were designated APB and APF (see Figure 2). ChemWest was instructed to analyze the samples for total tetra through octa dioxin/furan isomers, as well as 2, 3, 7, 8 TCDD and 2, 3, 7, 8 TCDF. The latter two parameters are considered the most toxic of all the dioxin/furan compounds.

The initial extraction took place on August 15, 1989, 33 days following sample collection. The samples were analyzed on September 14, 1989, 63 days after sample collection. Holding times established in Method 8280, SW-846, 3<sup>rd</sup> Edition, call for extraction within 30 days and analysis within 45 days. Therefore, the extraction time limit was exceeded by three days and the analysis time limit was exceeded by eighteen days.

The initial analysis revealed low internal standard recoveries caused by matrix interference. Since these results were not acceptable the laboratory re-extracted the samples on September 15, 1989 and re-analyzed the samples on September 27, 1989. The internal standard percent recoveries were all within an acceptable range.

In addition to holding times, the method blanks, internal standard percent recoveries, surrogate recoveries, initial calibration and continuing calibration data were all checked. Except for holding times, all QA/QC data were within the limits outlined in Method 8280, SW-846, 3<sup>rd</sup> Edition. The QA/QC Summary Sheet for the July 1989 ash samples is shown on page 9 of this report.

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QA/QC Summary Sheet--July 1989 Samples

QA/QC Review of PCDD/PCDF Data  
for ChemWest Ticket N° 4385

Holding Times: The samples were initially analyzed outside Method 8280, SW-846, 3<sup>rd</sup> Edition holding times. The samples had interference problems and were extracted again, cleaned up and analyzed again in order to get valid data.

Method Blanks: The method blank reported all target dioxins and furans as non-detected.

Internal Standard Recoveries: All internal standard recoveries ranged from 48% to 93%. SW-846 does not have control limits established.

Surrogate Recoveries: All surrogate recoveries ranged from 98% to 117%. SW-846 does not have control limits established.

Initial Calibration: All target compounds had mean RRF's greater than 0.70 and percent RSD's less than 15%.

Initial Calibration Ion Abundance Ratio Summary: All ratios for ion pairs were within control limits.

Continuing Calibration: All target compounds had RRF's greater than 0.70, %D's less than 15% (limit 0-30%) and all ratio's for ion pairs within control limits.

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### 3.2 November 1989 Samples

Ash samples collected on November 20, 1989 were designated ASH-B and ASH-F (see Figure 2). Special arrangements were made to ensure that the holding times would be adhered to by ChemWest. CompuChem transferred the samples to ChemWest under chain of custody with a note to alert ChemWest about the need to meet published holding times. ChemWest was instructed to analyze the samples for all 2, 3, 7, 8 PCDD and PCDF isomers (the most toxic isomers for which toxicity equivalents have been established), tetra through octa, as well as total tetra through octa dioxin/furan isomers.

The samples were initially extracted on December 4, 1989. Sample ASH-F was analyzed on January 12, 1990, and sample ASH-B was analyzed on January 17, 1990. The initial extractions were performed 14 days following sample collection which is well within the 30 day holding time, specified in Method 8280. ASH-F was analyzed 53 days following sample collection and ASH-B was analyzed 58 days following collection. The holding times for analysis was exceeded in both of these samples by eight days and thirteen days, respectively.

As with the July samples, the initial analysis for both November samples revealed low internal standard percent recoveries caused by matrix interference. ChemWest re-extracted the samples on January 17, 1990 and re-analyzed them on January 25, 1990. The internal standard percent recoveries for the re-analyzed samples were all within an acceptable range.

In addition to holding times, the method blanks, surrogate recoveries, internal standard percent recoveries, initial calibration and routine calibration data were all checked. Except for holding times, all QA/QC data were within the limits outlined in 8280, SW-846, 3<sup>rd</sup> Edition. The QA/QC Summary Page of the November 1989 ash samples is shown on page 11 of this report.

QA/QC Summary Sheet--November 1989 Samples

QA/QC Review of PCDD/PCDF Data  
for ChemWest Ticket N<sup>o</sup> 5054

Holding Times: The samples were initially analyzed outside Method 8280, SW-846, 3<sup>rd</sup> Edition holding times. The samples had interference problems and were again extracted, cleaned up and analyzed again in order to get valid data.

Method Blanks: The method blank associated with these samples had higher detection limits for certain compounds, relative to the samples. In addition, some internal standard area recoveries were low. Two additional method blank runs were included in the report that bracket these samples. These detection limits and recoveries were acceptable.

Internal Standard Percent Recovery: The 13C12-OCDD recovery for ASH-B was a little low (11.4%). No action should be taken since there are no documented control limits.

Surrogate Recovery: All surrogate recoveries were within acceptable limits.

Initial Calibration: All average RRF's had % RSD's less than 15% as required.

Routine Calibration: All 500ng RRF's had % D's less than 30% as required.

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## 4.0 RESULTS AND DISCUSSION

In this section the results for both sets of ash analyses will be presented as well as a discussion of the validity of these data. Specifically, the issue of holding times as they affect the analytical results will be considered. Lastly, an analysis of the results with respect to toxicity and potential risk will be presented.

### 4.1 Analytical Results

The results for both sets of ash samples are presented in Table 1. As described in section 3.1 only the totals for each isomer group were analyzed for in the July samples except for the two specific compounds 2,3,7,8 TCDD and 2,3,7,8 TCDF. Analyses for the November samples included isomer totals, 2378 TCDD, 2378 TCDF, as well as other 2378 isomers. Overall, the results for the July and November sample sets are in excellent agreement. Although the two sample sets can not be considered duplicates because they were sampled four months apart, the results were within the control limits used to evaluate field duplicates for soils. The limit is set at less than 100% relative percent difference (RPD). For the two sample sets the RPDs ranged from 0% to 79.7% as shown in Table 1. This consistency is a good indication of the accuracy of the analytical results.

The results in both sets of samples for tetra, penta, and hexa dioxin isomers, including 2378 TCDD, reportedly the most toxic isomer, were all below the detection limits indicated except for total hexa dioxin in the November sample from the ash pile east of the main facility building. The concentration in this sample was 1.7 ppb. However, the concentrations for the three isomers listed, also reported as potentially toxic, were all below the detection limit (<0.57 ppb). The majority of the remaining dioxin and furan compounds had concentrations in the low parts per billion range.

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Table 1

**Summary of Analytical Results--Ash  
Dioxins and Furans--July and November 1989  
C & D Recycling Site Remedial Investigation**

Parameter	Ash Pile East of Main Building			Ash Pile South of Old Furnace		
	7/89	11/89	RPD*	7/89	11/89	RPD*
Total TCDD	<0.47	<0.54	--	<0.29	<0.51	--
2378 TCDD	<0.73	<0.53	--	<0.35	<0.76	--
Total PeCDD	<0.77	<0.87	--	<0.52	<0.56	--
12378 PeCDD		<2.8			<1.1	
Total HxCDD	<2.0	1.7	--	<1.4	<0.96	--
123478 HxCDD		<0.57			<1.6	
123678 HxCDD		<0.57			<1.6	
123789 HxCDD		<0.57			<1.6	
Total HpCDD	7.3	7.3	0%	2.7	3.7	31.3%
1234678 HpCDD		3.6			1.9	
Total OCDD	14.4	11.4	23.3%	5.4	4.1	27.4%
Total TCDF	<4.9	5.9	--	4.3	10.0	79.7%
2378 TCDF	1.6	1.5	11.7%	1.4	2.4	52.6%
Total PeCDF	8.2	8.2	0%	5.9	10.8	58.6%
12378 PeCDF		0.55			0.80	
23478 PeCDF		0.72			1.5	
Total HxCDF	12.1	12.2	0.8%	6.6	9.9	40.0%
123478 HxCDF		4.2			3.6	
123678 HxCDF		1.4			1.1	
234678 HxCDF		0.49			<0.81	
123789 HxCDF		1.5			<0.81	
Total HpCDF	15.8	17.9	12.5%	6.4	9.4	38.0%
1234678 HpCDF		11.9			6.9	
1234789 HpCDF		2.1			<1.7	
Total OCDF	30.9	24.8	21.9%	7.2	5.1	34.1%

-- = Not applicable

< = Less than

\* = Relative Percent Difference

Results in parts per billion (ppb).

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#### 4.2 Holding Times

As indicated in section 3 the holding times for extraction and analysis were exceeded for both sets of ash samples. It is highly doubtful that this has in any way affected the quality of the analytical results. In conversations with analytical personnel from both ChemWest and USEPA (personal communication, January 1990) HART was informed that the holding times set forth in Method 8280 are a contractual requirement and have no technical basis. From the point of view of sample stability, the chemical character of the ash samples would not change as a result of the transfer from the ash pile itself to a sealed, chilled sample jar. No changes are to be expected during sample storage because these compounds possess very low solubilities and are bound tightly to the ash particles. In any event, the ash has been sitting on the Site for years. Since all of the other QA/QC parameters were within acceptable limits, and the fact that both sets of results are in excellent agreement, the results can be considered accurate and valid.

#### 4.3 Potential Toxicity

Although total dioxin/furan concentrations correlate well between the two sets of data it is not technically correct to calculate toxic equivalents for dioxins and furans unless the specific isomers are analyzed. The current USEPA methodology for evaluating dioxins and furans is outlined in the document entitled *1989 Update to the Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-Dioxins and Dibenzo-p-Dibenzofurans (CDDs and CDFs)* (USEPA, 1989). Basically, the method equates the concentration of individual isomers to the isomer which USEPA considers as the most toxic (2,3,7,8-Tetrachloro Dibenzo-p-Dioxin (TCDD)) even when TCDD is not present. Identified isomers of dioxins and furans are expressed as toxicity equivalents (TEQs) which are the product of the reported isomer concentration and a toxic equivalency factor (TEF). For example, the compound 1,2,3,7,8 pentachloro dibenzofuran is known to be 20 times less toxic than 2378 TCDD. Its TEF, then is 0.05 (1 divided by 20). If a sample contained 30 PPB of 1,2,3,7,8 PeCDF, the toxicity of that sample would be the same as if the sample contained 1.5 ppb of 2378 TCDD (30 ppb times 0.05).

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The USEPA has established TEFs for the dioxin and furan compounds which it considers to be potentially toxic. These TEFs are shown in Table 2 and the values have been used to calculate a TEQ for the results from the November 1989 ash samples. The TEQ for each of the compounds present in the samples have been added to determine the total potential toxicity of each ash sample relative to the toxicity of 2378 TCDD. As shown in Table 2, the USEPA Toxicity Equivalent for ASH-B is 1.5087 ppb and for ASH-F is 1.5972 ppb. These TEQs are very low and barely exceed the standard of 1 ppb for residential soils as promulgated by the Centers for Disease Control (USEPA, Personal Communication, January 18, 1990).

At this time all ash piles are within the fenced area of the Site. In addition, all ash piles are covered with one foot of soil and Visqueen. Since dioxins and furans are essentially insoluble and because the soil and Visqueen covering prevents infiltration of precipitation or dispersion of the ash by wind, the potential for migration of ash has been effectively eliminated. Therefore, any potential risk to residents in the vicinity of the Site under current conditions has been effectively eliminated.

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TABLE 2

SUMMARY OF VALID ANALYTICAL RESULTS FOR  
CHLORINATED DIBENZO-P-DIOXINS AND  
CHLORINATED DIBENZO-P-FURANS DETECTED  
IN ASH AND CALCULATION OF TOXIC EQUIVALENTS

C & D RECYCLING SITE

<u>Compound</u>	<u>Ash B (1)</u> <u>(ug/kg)</u>	<u>TEF (2)</u>	<u>Toxicity</u> <u>Equivalents</u> <u>(ug/kg) (3)</u>	<u>Ash F (1)</u> <u>(ug/kg)</u>	<u>TEF (2)</u>	<u>Toxicity</u> <u>Equivalents</u> <u>(ug/kg) (3)</u>
2,3,7,8 - TCDD	-	1	-	-	1	-
Other TCDDs	-	0	-	-	0	-
2,3,7,8 - PeCDD	-	0.5	-	-	0.5	-
Other PeCDDs	-	0	-	-	0	-
2,3,7,8 - HxCDDs	-	0.1	-	-	0.1	-
Other HxCDDs	1.7	0	0	-	0	-
2,3,7,8 - HpCDD	3.6	0.01	0.036	1.9	0.01	0.019
Other HpCDDs	3.7	0	0	1.8	0	0
OCDD	11.4	0.001	0.0114	4.1	0.001	0.0041
TOTAL CDDs			0.0474			0.0231
2,3,7,8 - TCDF	1.5	0.1	0.15	2.4	0.1	0.24
Other TCDFs	4.4	0	0	7.6	0	0
1,2,3,7,8 - PeCDF	0.55	0.05	0.0275	0.8	0.05	0.04
2,3,4,7,8 - PeCDF	0.72	0.5	0.36	1.5	0.5	0.75
Other PeCDFs	6.93	0	0	8.5	0	0
2,3,7,8 - HxCDFs	7.59	0.1	0.759	4.7	0.1	0.47
Other HxCDFs	4.61	0	0	5.2	0	0
2,3,7,8 - HpCDFs	14.0	0.01	0.14	6.9	0.01	0.069
Other HpCDFs	3.9	0	0	2.5	0	0
OCDF	24.8	0.001	0.0248	5.1	0.001	0.0051
TOTAL CDFs			1.4613			1.5741
TOTAL TEQs			1.5087			1.5972

Notes:

(1) November 20, 1989 Sampling data was used in the calulations.

(2) TEF = Toxic Equivalency Factor; Source: USEPA, March, 1989. 1989 Update to the Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-Dioxins and Dibenzo-p-Dibenzofurans (CDDs and CDFs). Risk Assessment Forum. EPA/625/3-89/016.

(3) Toxicity Equivalent = CDD or CDF Concentration X TEF.

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Canadian Council of Resource and Environment Ministers, 1986. Dioxins and Furans: Environment Canada.

USEPA, 1989. 1989 Update to the Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-Dioxins and Dibenzo-p-Furans (CDDs and CDFs): Risk Assessment Forum, EPA/625/3-89/016.

USEPA, 1986. Test Methods for Evaluating Solid Waste, Volume 1B: Laboratory Manual, Physical/Chemical Methods, SW-846, 3<sup>rd</sup> Edition.

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